



## Electrochemical performance of rechargeable Li/LiFePO<sub>4</sub> cells with ionic liquid electrolyte: Effects of Li salt at 25 °C and 50 °C



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### HIGHLIGHTS

- LiTFSI is better than LiPF<sub>6</sub> as solute in BMP–TFSI IL for Li/LiFePO<sub>4</sub> cells.
- LiTFSI concentration in IL greatly affects the cell performance.
- At 50 °C, the cell performance with IL is close to that with organic electrolyte.
- The cell shows little decay after 100 cycles at 50 °C in the IL electrolyte.
- IL electrolyte is ideal for high-temperature and high-safety applications.

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### ABSTRACT

Lithium hexafluorophosphate (LiPF<sub>6</sub>) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) are used as Li salts in butylmethylpyrrolidinium–bis(trifluoromethanesulfonyl)imide (BMP–TFSI) ionic liquid (IL) electrolyte for Li/LiFePO<sub>4</sub> cells. This kind of IL electrolyte shows high thermal stability (>400 °C) and non-flammability, and is thus ideal for high-safety applications. At 25 °C, a maximum capacity of 113 mAh g<sup>-1</sup> (at 0.1 C) is found for LiFePO<sub>4</sub> in the IL with 0.5 M LiTFSI. An excessive LiTFSI concentration leads to a capacity decrease due to reduced electrolyte ionic conductivity. At 50 °C, the measured capacity and rate capability are significantly improved compared to those at 25 °C. With 1 M LiTFSI-doped IL electrolyte (the optimum concentration at 50 °C), a capacity of 140 mAh g<sup>-1</sup> is found at 0.1 C and 45% of the capacity can be retained when the rate increases to 5 C, values which are comparable to those found in a traditional organic electrolyte. In the IL electrolyte, the LiFePO<sub>4</sub> electrode shows better cyclic stability at 50 °C than it does at 25 °C; this trend is opposite to that found in the organic electrolyte. At 50 °C, there is negligible capacity loss of LiFePO<sub>4</sub> after 100 charge–discharge cycles in 1 M LiTFSI-doped BMP–TFSI IL electrolyte.

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### 1. Introduction

Lithium (Li)-based batteries are the dominant charge storage units for consumer portable electronic devices [1]. They are also the most promising option for next-generation hybrid and electric vehicles [2–5], and are being considered for grid-scale energy storage for renewable wind and solar power [6]. In addition to

battery performance, safety issues are critical for Li batteries to be extended to further applications [7]. Organic electrolytes, which are typically used in Li batteries, are responsible for the major safety problems as they have poor thermal stability, high flammability, and low heat capacity (which facilitates localized heating) [8]. These electrolytes also pose potential environmental hazards due to their volatility and toxicity [9]. Therefore, a safer and greener alternative electrolyte that can optimize battery performance is highly desired.

Ionic liquids (ILs), characterized by intrinsic ionic conductivity, large electrochemical windows, excellent thermal stability, non-volatility, and non-flammability [10–14], are promising for use as electrolytes for Li batteries. Since their physical and chemical properties can be designed by selecting the appropriate cation/

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anion combination [15], ILs are characterized as task-specific electrolytes that can endow Li batteries with the desired functionality. Among various IL systems, butylmethylpyrrolidinium–bis(trifluoromethylsulfonyl)imide (BMP–TFSI) has attracted lots of attention because its cathodic stability limit (associated with the reduction of  $\text{BMP}^+$ ) is beyond the Li plating/stripping reaction and  $\text{TFSI}^-$  can withstand a high potential (>5.5 V vs. Li) [16]. The inherent limitation of IL electrolyte is the relatively high viscosity compared to that of conventional organic electrolyte, making it suitable for only low-C-rate applications at room temperature. Recently, Castiglione et al. [17] found a large enhancement of  $\text{Li}^+$  mobility in IL with increasing temperature. However, the effects of temperature on battery performance with IL electrolyte have rarely been systematically investigated in the literature. The present study thus evaluates the feasibility of using IL electrolyte for elevated-temperature applications.

Li salts are dissolved in electrolytes to endow the  $\text{Li}^+$  transport ability. The effects of the type and concentration of Li salts in organic electrolyte, which are critical to battery performance, have been extensively reported [18,19]. However, there have been no reports on the effects of  $\text{Li}^+$  concentration in BMP–TFSI IL. In the present study, Li/LiFePO<sub>4</sub> cells incorporating BMP–TFSI-based IL electrolytes are evaluated. Two types of Li salt, namely LiPF<sub>6</sub> and LiTFSI, are used and the resulting battery properties are compared. The concentration of the latter salt is varied from 0.1 M to 1.0 M to modify the physicochemical characteristics of the IL electrolyte at 25 °C and 50 °C. For comparison, a conventional organic electrolyte (1 M LiPF<sub>6</sub> in EC:DEC solvent (1:1, v/v)) is adopted in an identical cell. Thermal stability and flammability evaluations are also performed to compare the durability and safety of the IL and organic electrolytes.

## 2. Experimental procedure

### 2.1. Preparation of LiFePO<sub>4</sub> and ionic liquid electrolyte

Carbon-coated LiFePO<sub>4</sub> powder was prepared using a carbo-thermal reduction method at 700 °C involving a mixture of ferric oxide (99 wt%, Taiwan Polychem Co. Ltd.), ammonium dihydrogen phosphate (99 wt%, First Chemical Works Co. Ltd.), and lithium carbonate (99 wt%, First Chemical Works Co. Ltd.) in a stoichiometric molar ratio. In the process, polyethylene glycol (PEG, M.W. = 6000, Huacheng Industrial Co. Ltd.) was used as a reduction agent as well as a carbon source. The detailed preparation procedures can be found in a previous paper [20]. BMP–TFSI IL was prepared and purified following a published method [21]. The IL was washed with dichloromethane (99 wt%, SHOWA), filtrated to remove precipitates, and then vacuum dried at 100 °C for 12 h before use. Two kinds of Li salt, LiPF<sub>6</sub> (99.9 wt%, Strem Chemicals Inc.) and LiTFSI (98 wt%, Tokyo Chemical Industry Co. Ltd.), were dissolved in the BMP–TFSI IL, respectively. Each mixture was continuously stirred by a magnetic paddle for 24 h to ensure uniformity. A conventional organic electrolyte, consisting of 1:1 (by volume) ethylene carbonate (99 wt%, Alfa Aesar) and diethyl carbonate (99 wt%, Alfa Aesar) as co-solvent and 1 M LiPF<sub>6</sub> solute, was also prepared for comparison. All the chemicals were stored and handled in an argon-filled glove box (Innovation Technology Co. Ltd.), where both the moisture and oxygen contents were maintained below 1 ppm.

### 2.2. Cell assembly

A cathode slurry was prepared by mixing 75 wt% synthesized LiFePO<sub>4</sub> powder, 20 wt% carbon black, and 5 wt% poly(vinylidene fluoride) in N-methyl-2-pyrrolidone solution. The slurry was

pasted onto Al foil and vacuum dried at 110 °C for 2 h. Then, the cathode electrode was roll-pressed and punched to match the required dimensions of a CR2032 coin cell. Li foil and a Celgard polypropylene membrane were used as the anode and the separator, respectively. The assembly of the coin cell was performed in the argon-filled glove box.

### 2.3. Material and electrochemical characterization

The morphology of the synthesized LiFePO<sub>4</sub> was examined with a scanning electron microscope (SEM; FEI Inspect F50). An X-ray diffractometer (XRD; Shimadzu XRD-6000) with a Cu target was used to analyze the crystal structure. The X-ray detector was scanned in a diffraction angle range of 15°–65° at a speed of 1° min<sup>-1</sup>. A thermogravimetric analyzer (TGA; Perkin–Elmer TGA7) was employed to examine the thermal stability of the electrolytes. The samples were heated from room temperature to 550 °C at a heating rate 5 °C min<sup>-1</sup> under a nitrogen atmosphere. The electrolyte flammability was tested under air according to an established method in the literature [22]. Briefly, glassy fiber filters were used to adsorb the electrolytes and then burned with an electric Bunsen burner (with a distance of 120 mm between the sample and the burner). The electrolyte conductivity was measured using a conductivity meter (TetraCon 325) in the glove box to avoid oxygen

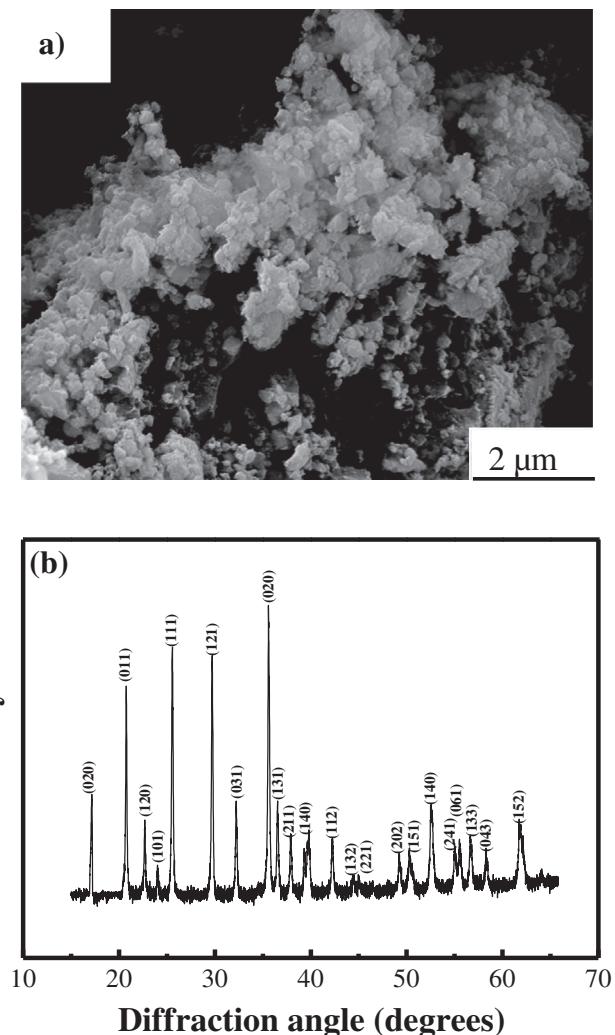
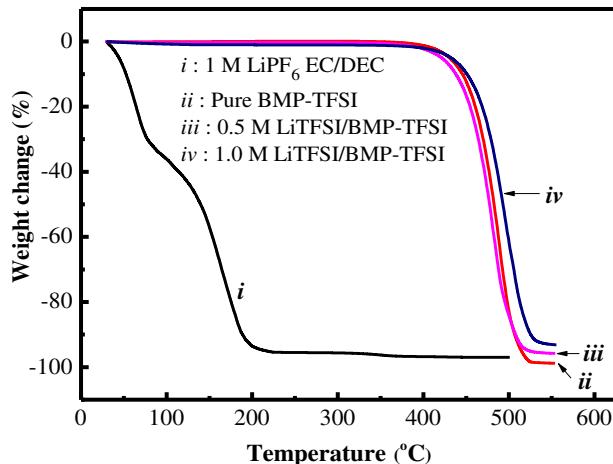


Fig. 1. (a) SEM image and (b) XRD pattern of LiFePO<sub>4</sub> powder synthesized using PEG-assisted carbothermal reduction method.

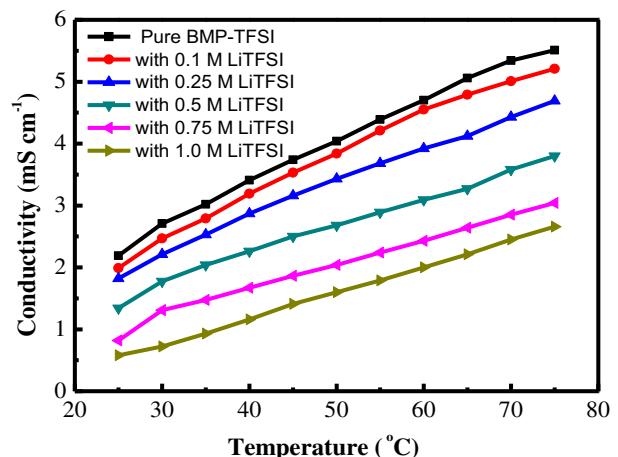


**Fig. 2.** TGA data of BMP–TFSI IL with various concentrations of LiTFSI. A conventional organic electrolyte (1 M LiPF<sub>6</sub> in EC:DEC (1:1, v/v) solvent) is also presented. The measurements were performed at a heating rate of 5 °C min<sup>-1</sup> under a nitrogen atmosphere.

and moisture interference. The charge–discharge performances (such as capacity, high-rate capability, and cyclic stability) of the Li/LiFePO<sub>4</sub> cells with various electrolytes at 25 °C and 50 °C were evaluated using a battery tester (Arbin BT-2043).

### 3. Results and discussion

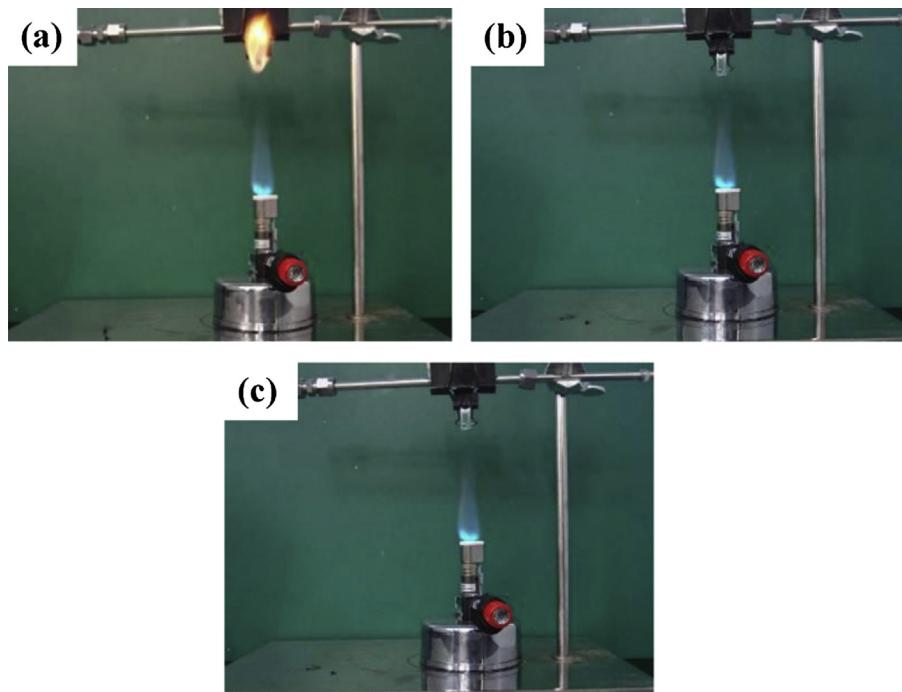
A typical SEM image of the LiFePO<sub>4</sub> powder synthesized by a PEG-assisted carbothermal reduction method is shown in Fig. 1(a). The agglomerated cluster in the micrograph (~10 µm in diameter) consists of numerous nanograins. The primary particle size was in a range of 100–200 nm, which is smaller than that of the powder synthesized using different processes [22–26]. This can be attributed to the presence of PEG during the preparation process refining the morphology and size of the powders [27]. It has been confirmed



**Fig. 4.** Temperature-dependent ionic conductivity of pure BMP–TFSI IL and BMP–TFSI IL doped with various concentrations of LiTFSI.

that a small size of LiFePO<sub>4</sub> can shorten the Li<sup>+</sup> diffusion pathway and thus improve the charge–discharge performance of the electrode [28]. Fig. 1(b) presents the XRD pattern of the obtained powder. All the diffraction peaks can be attributed to a single olivine phase with an orthorhombic structure (JCPDS card no. 40-1499). This result confirms that the Fe<sub>2</sub>O<sub>3</sub> precursor was completely reduced (by PEG) and that no impurity phases formed during the synthesis. It was noted that no diffraction signal from the carbon coating was found. The surface carbon film (which can be recognized with an X-ray photoelectron spectrometer; see supplementary data) was either too thin or its crystallinity was too low, and thus it could not be detected with XRD.

Fig. 2 exhibits the TGA data of various IL electrolytes and the conventional organic electrolyte. The BMP–TFSI-based ILs show a decomposition temperature of approximately 400 °C, indicating high thermal stability. It was found that the residual weights after the 550 °C tests increased with increasing LiTFSI concentration.



**Fig. 3.** Flammability tests of (a) 1 M LiPF<sub>6</sub> in EC:DEC (1:1, v/v) organic electrolyte, (b) plain BMP–TFSI IL, and (c) 1 M LiTFSI-doped BMP–TFSI IL. Glassy fiber filters were used to adsorb the electrolytes and were then heated with electric Bunsen burners.

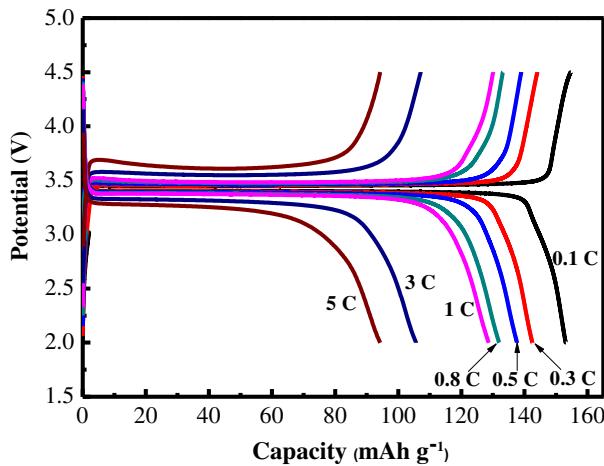


Fig. 5. Charge–discharge voltage profiles of Li/LiFePO<sub>4</sub> cell with organic electrolyte (1 M LiPF<sub>6</sub> in EC:DEC (1:1, v/v)) recorded at various C rates at 25 °C.

This is associated with the fact that the decomposition product of LiTFSI (as a solid) remained in the TGA crucible at 550 °C. In contrast, the traditional organic electrolyte shows a significant weight loss of ~40% when the temperature reached 100 °C, at which point the carbonate solvent vigorously evaporated and the LiPF<sub>6</sub> solute started to decompose to LiF and PF<sub>5</sub> [29,30]. These results clearly reveal that IL electrolytes are more suitable for high-temperature applications.

The flammability of the IL and organic electrolytes (typically 0.1 g) was tested under air. As shown in Fig. 3(a), the BMP–TFSI IL did not show any ignition, even when directly exposed to fire. It was found that the LiTFSI content in the IL had no influence on the results (Fig. 3(b)). In contrast, the organic electrolyte ignited immediately and burned rather violently (Fig. 3(c)). When the burner was removed, the average self-extinguishing time (for 6 samples) was found to be ~60 s g<sup>-1</sup>. The non-flammability of the IL electrolytes is ideal for high-safety battery applications.

The ionic conductivity of the IL electrolyte, a key factor that affects battery performance, was acquired as a function of the LiTFSI concentration at temperatures between 25 °C and 75 °C. Fig. 4 shows the results. At 25 °C, the measured ionic conductivity of plain BMP–TFSI IL was 2.2 mS cm<sup>-1</sup>, which is consistent with a previously reported value [31]. With LiTFSI concentrations of 0.1, 0.25, 0.5, 0.75, and 1 M, the IL conductivity decreased to 2.0, 1.8, 1.3, 0.8, and 0.4 mS cm<sup>-1</sup>, respectively. The reduction in the electrolyte conductivity is attributed to the increased viscosity and the enhanced ion–ion interaction due to the introduction of foreign ions [32]. Also shown in Fig. 4 is the trend that the IL conductivity increases (regardless of the LiTFSI concentration) with increasing temperature. For example, the ionic conductivity of the 1 M LiTFSI-doped IL monotonically increased up to 2.7 mS cm<sup>-1</sup> at 75 °C. An increase in temperature promoted the dissociation of the Li salt and improved the ion mobility, enhancing the ionic conductivity of the IL electrolyte.

Fig. 5 shows the charge–discharge voltage profiles of the Li/LiFePO<sub>4</sub> cell recorded at various C rates in the organic electrolyte. The maximum capacity (at 0.1 C) of LiFePO<sub>4</sub> was approximately 153 mAh g<sup>-1</sup>, which is close to the theoretical value (170 mAh g<sup>-1</sup>) [33]. This indicates that the synthesized electrode is of high quality. Fig. 6(a) and (b) compares the electrochemical properties of cells incorporating BMP–TFSI electrolyte with 0.5 M LiTFSI and 0.5 M LiPF<sub>6</sub>, respectively. At 0.1 C, the measured discharge capacities were 113 mAh g<sup>-1</sup> and 109 mAh g<sup>-1</sup>, respectively. The performance difference between the two electrolytes became more significant at

0.3 C; the capacity with LiTFSI was 88 mAh g<sup>-1</sup>, whereas that with LiPF<sub>6</sub> was considerably lower at 64 mAh g<sup>-1</sup>. The introduction of a dissimilar type of anion (PF<sub>6</sub><sup>-</sup>) complicates the ion–ion interaction, thus increasing the viscosity and hindering the ionic transport in the IL electrolyte [34,35]. LiTFSI-doped BMP–TFSI IL has been reported to have a higher conductivity than that of LiPF<sub>6</sub>-doped BMP–TFSI IL [36]. It was also proposed that Li salt with the same anion as the base IL is preferred, since a higher solubility can be achieved [15,17]. Moreover, the present study found that the decomposition temperature of LiTFSI is ~450 °C, which is much higher than that (below 100 °C) for LiPF<sub>6</sub>. Based on the above analyses, LiTFSI is more suitable than LiPF<sub>6</sub> as the Li<sup>+</sup> source in BMP–TFSI IL electrolyte for Li battery applications. This is the first study to compare the effects of Li salt type on the electrochemical performance of Li/LiFePO<sub>4</sub> cells with IL electrolytes.

It was found that the LiTFSI concentration in the IL electrolyte substantially affects cell performance. As shown in Fig. 7(a), the measured discharge capacities of LiFePO<sub>4</sub> (at 0.1 C and 25 °C) were 84, 93, and 113 mAh g<sup>-1</sup> when the incorporated LiTFSI was 0.1, 0.25, and 0.5 M, respectively. A sufficient amount of Li<sup>+</sup> is necessary to promote the lithiation/delithiation reaction of LiFePO<sub>4</sub>. However, an excessive addition of the Li salt had an adverse effect on the capacity. When the concentration of LiTFSI reached 1.0 M, the discharge capacity decreased to 91 mAh g<sup>-1</sup>. This can be attributed to reduced electrolyte conductivity, as shown in Fig. 4. There is trade off between the increase in the number of working ions and

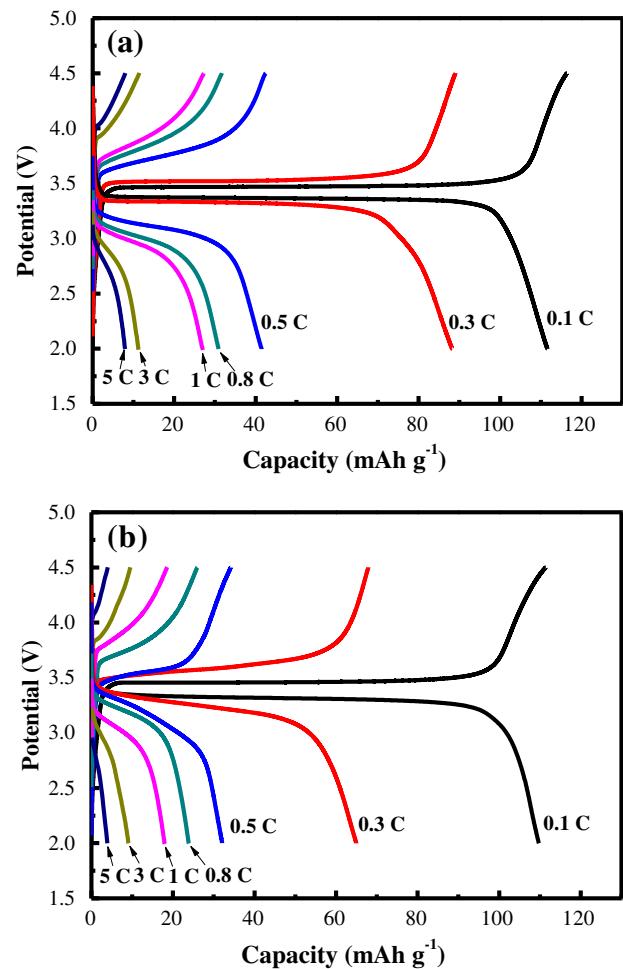
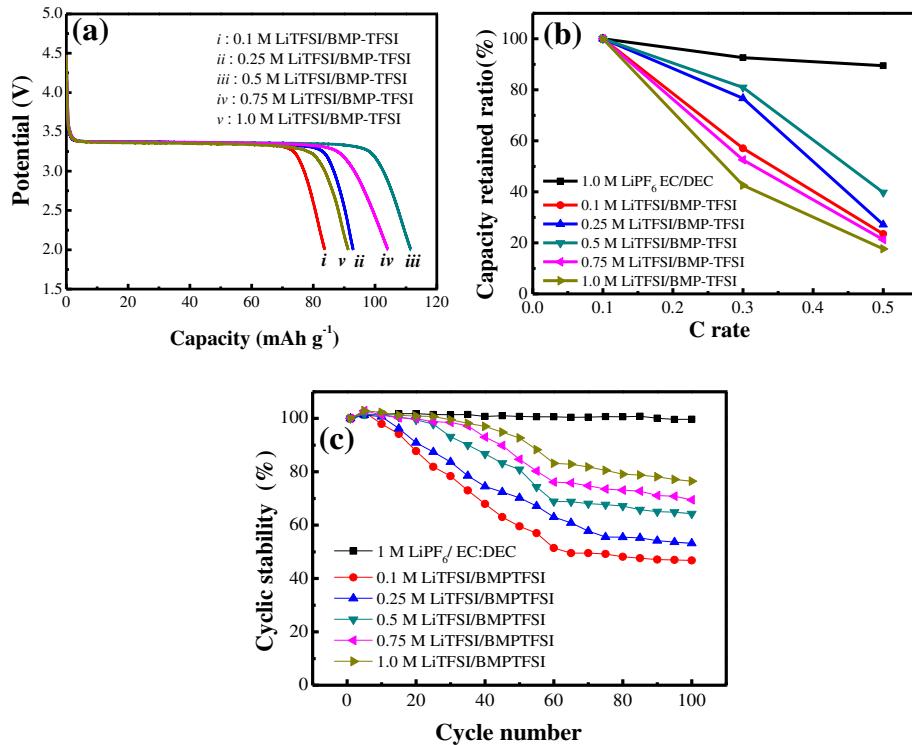


Fig. 6. Charge–discharge voltage profiles of Li/LiFePO<sub>4</sub> cells incorporating BMP–TFSI electrolytes with (a) 0.5 M LiTFSI and (b) 0.5 M LiPF<sub>6</sub> recorded at various C rates at 25 °C.



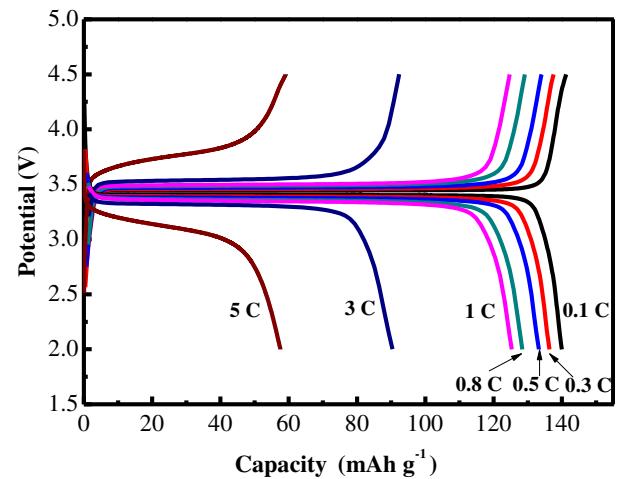
**Fig. 7.** (a) Discharge curves at 0.1 C, (b) capacity retained ratios at various C rates compared to that obtained at 0.1 C, and (c) cyclic stability of Li/LiFePO<sub>4</sub> cells incorporating BMP-TFSI electrolytes with various concentrations of LiTFSI. The data were acquired at 25 °C.

the decrease in electrolyte conductivity (both due to the introduction of LiTFSI); the optimal LiTFSI concentration is  $\sim 0.5$  M. Fig. 7(b) shows the capacity retained ratio of LiFePO<sub>4</sub> at various C rates compared to that obtained at 0.1 C in various IL electrolytes. As demonstrated, the highest retained ratio was found for the 0.5 M LiTFSI-doped IL. However, due to the relatively high viscosity and low conductivity of the IL electrolytes, the high-rate performance is inferior to that of a similar cell with the conventional organic electrolyte.

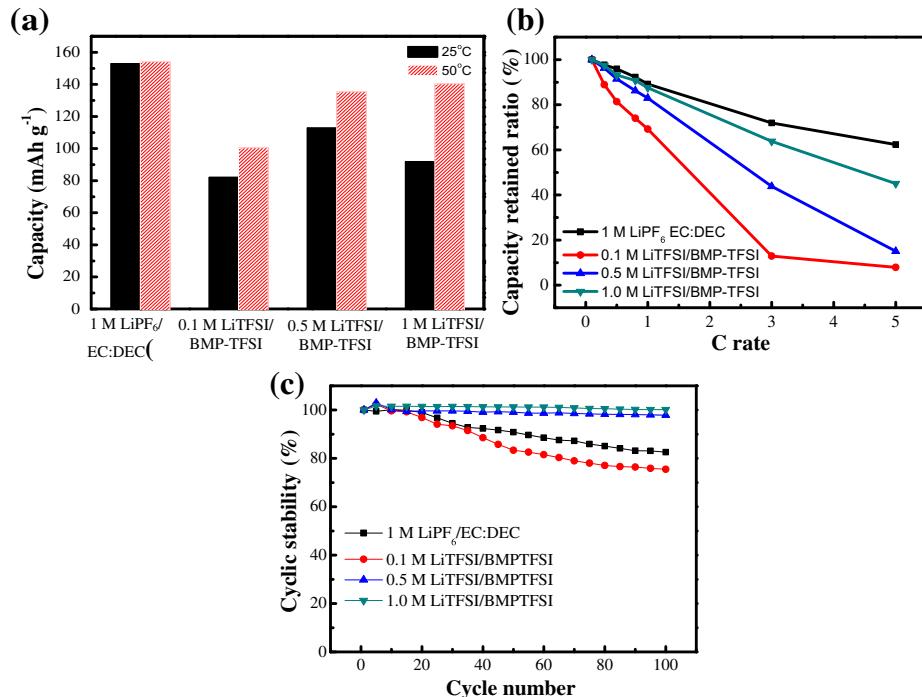
Fig. 7(c) shows the cyclic stability of cells with various electrolytes at 25 °C. With increasing LiTFSI concentration in the IL electrolyte, the electrochemical stability clearly improved. After 100 cycles, the capacity retained ratio (compared to the initial capacity) increased from 47% to 78% when the LiTFSI concentration was increased from 0.1 M to 1 M. A low LiTFSI concentration resulted in a small Li<sup>+</sup> transference number in the IL, leading to a large polarization and thus a rapid deterioration of the electrode during charge–discharge cycling [37]. As also shown in Fig. 7(c), a satisfactory cell durability was found with the organic electrolyte. The IL electrolyte needs to be further modified (e.g., redesign of the constituent cations and anions and/or introduction of additives) to improve its room-temperature properties.

Increasing the temperature from 25 °C to 50 °C caused a substantial performance change of the IL electrolyte. Fig. 8 shows the voltage profiles of the Li/LiFePO<sub>4</sub> cell recorded at 50 °C with various C rates in 1 M LiTFSI-doped IL electrolyte. Compared to Fig. 6 (data for 25 °C), a clear charge–discharge performance improvement can be recognized, which is associated with a significant enhancement of Li<sup>+</sup> mobility at elevated temperature [17]. Fig. 9(a) summarizes the measured LiFePO<sub>4</sub> capacities (at 0.1 C) in various electrolytes at 25 °C and 50 °C. While the cell capacity in the organic electrolyte remained almost unchanged, a temperature rise led to considerable capacity increases in the IL electrolytes. At 50 °C, with the LiTFSI concentration in the IL increased from 0.1 M to 0.5 M and 1.0 M, the

capacities were 100, 135, and 140 mAh g<sup>-1</sup>, respectively, approaching the value of 154 mAh g<sup>-1</sup> obtained for the organic electrolyte. Fig. 9(b) compares the rate capability in various electrolytes at 50 °C. As shown, the cell with 1 M LiTFSI-doped IL has the best high-rate performance; at a high rate of 5 C, more than 45% of the capacity (at 0.1 C) can be retained, which is comparable to that for the organic electrolyte. It was found that further increasing the LiTFSI concentration to 1.5 M did not significantly change the cell capacity and rate capability. At 50 °C, the viscosity increase of the IL due to Li salt introduction was suppressed; as a result, the optimal LiTFSI concentration is approximately 1 M, which is higher than  $\sim 0.5$  M for 25 °C. According to the present data, at 50 °C, which is often encountered during applications, a comparable cell



**Fig. 8.** Charge–discharge voltage profiles of Li/LiFePO<sub>4</sub> cell incorporating BMP-TFSI electrolyte with 1 M LiTFSI recorded at various C rates at 50 °C.



**Fig. 9.** (a) Comparison of measured LiFePO<sub>4</sub> capacities (at 0.1 C) in various electrolytes at 25 °C and 50 °C. (b) Capacity retained ratios at various C rates and (c) cyclic stability of Li/LiFePO<sub>4</sub> cells incorporating BMP-TFSI electrolytes with various concentrations of LiTFSI (at 50 °C).

performance (to that of traditional organic-electrolyte cells) can be achieved by appropriate control of the LiTFSI concentration in the IL electrolyte. Of note, the latter electrolyte is more stable and safer, as confirmed in Figs. 2 and 3.

Fig. 9(c) shows the cyclic stability of the Li/LiFePO<sub>4</sub> cells with various electrolytes evaluated at 50 °C. With the organic electrolyte, an ~18% capacity loss was found after 100 cycles, mainly due to undesirable electrode/electrolyte interactions and evaporation of the electrolyte at elevated temperature [38]. The cyclability gradually improved as the LiTFSI concentration in the IL electrolyte was increased from 0.1 M to 1 M. Specifically, in the 1 M LiTFSI-doped IL electrolyte, almost no capacity decay was found after 100 charge–discharge cycles. A sufficient amount of Li<sup>+</sup> is required to facilitate the charge-compensation reaction for LiFePO<sub>4</sub> and thus to ensure ideal electrode durability in the IL electrolyte. The non-volatility (thus no evaporation problem) and chemical benignity (thus low reactivity toward electrodes) of IL explain the great cyclic stability at 50 °C. Compared to Fig. 7(c), cyclability in the IL electrolytes significantly improved at higher temperature; this trend is opposite to that found for the organic electrolyte. Elevating the temperature increases the Li<sup>+</sup> transference number in the IL electrolyte [39] and thus minimizes the possible intercalation/deintercalation of BMP<sup>+</sup> and TFSI<sup>-</sup> in LiFePO<sub>4</sub>, improving electrode durability. The above results clearly indicate that IL electrolyte with an appropriate concentration of LiTFSI is promising for high-temperature applications, especially when the cell cycle life is a major concern.

#### 4. Conclusion

The high decomposition temperature (>400 °C) and non-flammability of BMP-TFSI-based IL make it a promising electrolyte for use in high-safety Li batteries. LiTFSI is more suitable than LiPF<sub>6</sub> as the solute in the IL electrolyte for Li/LiFePO<sub>4</sub> cells. The LiTFSI concentration in the IL greatly affects the capacity, rate capability, and cycle life of the LiFePO<sub>4</sub> electrode. At 25 °C, a

compromise between the number of working ions and the electrolyte conductivity results in an optimal LiTFSI concentration of ~0.5 M, which leads to a capacity of 113 mAh g<sup>-1</sup> (at 0.1 C). With the temperature at 50 °C, the charge–discharge performance of the cell with IL electrolytes significantly improved, coming close to that found with the traditional organic electrolyte. With the optimal LiTFSI concentration (i.e., 1 M at 50 °C), a capacity of 140 mAh g<sup>-1</sup> was obtained at 0.1 C and 45% of the capacity can be retained when the rate is increased to 5 C. In the IL electrolyte, the LiFePO<sub>4</sub> electrode shows little decay after 100 cycles at 50 °C. IL electrolyte with an appropriate concentration of LiTFSI is thus ideal for high-temperature applications.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2013.05.014>.

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